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Assessment of Heavy Metals Level of Soil in Kakuri Industrial Area of Kaduna, Nigeria

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Authors' contributions

This work was done in collaboration between all authors. Literature search and the first drafted manuscript were carried out by author EBA. Manuscript was reviewed and corrected by author SEA. All sampling and experiments were carried out by author SAE. All authors read and approved the final manuscript.

Article Information

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Original Research Article

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ABSTRACT

Aim: To determine the level and distribution of Zn, Cu, Ni, Cr, Pb, Hg and V from soils in the vicinities of Kakuri industrial area of Kaduna state, Nigeria.

Study Design: To compare the soil heavy metal concentrations with regulatory standard values permitted by the Nigerian environmental guideline as well as international standards and also subject the data to descriptive analysis to determine the Geo-accumulation index (I_{geo}) and contamination factor (C_i) .

Place and Duration of Study: Department of Chemistry, Ahmadu Bello University Zaria between February 2012 and July 2013.

Methodology: Twenty six soil samples at 0 to 10cm and 10 to 20cm depths from twelve (12) sample locations and two control samples was collected on the same day at Kakuri industrial area of Kaduna, Nigeria. The total concentrations of Cu, Zn, Pb, Cd Ni, Hg and V was determined using XRF spectrophotometer. Organic matter content (OM), pH, calcium carbonate and particle size distribution of the soil samples were also determined.

___ Results: The mean concentrations (in mgkg⁻¹) of Zn, Cu, Ni, Cr, Pb, Hg and V are 100.5±19.82, 60.02±3 .60, 26.25±6.44, 42.42±5.21, 32.00±1.68, 28.80±9.35 and 73.08±3.52 respectively. The

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metal concentrations (in mgkg⁻¹) ranged: Zn, 20-420; Cu, 26-110; Ni, 9-72; Cr, 22-157; Pb, 27-34; Hg, 10-60 and V, 47-120. Zn and Cu correlated positively with pH with values +0.41643 and +0.64447 respectively. Zn and Cu (+0.6142) and also Zn and Hg (+0.6377) had strong correlation which signifies the same source(s) in the soil. The contamination factor C_f values 1.31, 1.40 and 1.70 for Zn, Cu and Pb respectively falls under the classification $1 \leq C_f < 3$ indicates the soil is considerably contaminated but the $I_{\text{geo}} \le 1$ for all sample locations with the exception of KGW with $1 < I_{\text{geo}} \leq 2$.

Conclusion: Significant spatial variation in concentrations was observed for all metals across the locations and the degree of pollution varies with the level of industrial activities but were all within tolerable limit. The contamination factor C and I_{geo} index confirms the soil is uncontaminated.

Keywords: Soil; heavy metals; geo accumulation index; accumulation factor; XRF; kakuri, soil contamination.

1. INTRODUCTION

Heavy metals are common environmental pollutants and are released into soils from natural or anthropogenic sources. The main natural sources of metals in soils are weathering of parent material and soil erosion [1]. The anthropogenic sources are associated mainly with industrial activities such as metal finishing, paint pigment and battery manufacturing, leather tanning, mining activities, foundries and smelters, diffuse sources e.g., piping, constituents of products, combustion by-products, traffic emissions and other human activities like urban composts and municipal waste water sludge depositions and use of pesticides and phosphate fertilizers [2,3].

Soils are the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation [4] and the total concentration of heavy metals in soil persist for a long time after their introduction [5]. Changes in their chemical forms (speciation) and bioavailability are, however, possible.

The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants [6]. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems [7,8].

It is worthy of note that the major industrial activities in Kakuri industrial area has declined following the closure of some textiles industries. However there has been a tremendous increase in population and vehicular traffic, as well as the creation of a variety of ancillary activities such as vehicle repairs, vulcanizer, welders, autoelectricians, battery chargers etc. These activities result to heavy metals contamination of waterways and are subsequently deposited into nearby soils. There is therefore need for a continuous monitoring of level of heavy metal in the area in order to keep a check on the environment and to provide data for future research works.

2 MATERIALS AND METHODS

Soil samples were collected from twelve (12) selected locations namely United Textile road
(UNT). Railway Down Quarters (RDQ). Railway Down Quarters (RDQ), Chanchengi area (CCG), KTL road (KTL), Arewa Textiles road (ART), Ahmed Thalib road (AHT), DIC road (KGW), NBC road (NBC), Peugeot automobile road (PGA), Nocaco road (NCC), IBBI area (IBB) and Sunglass avenue (SNG) at 0 to 10cm and 10 to 20cm in Kakuri industrial area. The sampling sites are shown in (Fig. 1).

The soil surface was cleared with a hand trowel to a depth of approximately 10cm to 20cm before the samples were collected using a stainless steel spoon at 10 to 20cm depth. After every collection, the hand trowel and spoon were washed with soap and rinsed with distilled water to avoid sample contamination [9]. Five soil samples from each sampling location were randomly collected and pooled together to form a composite from each of the sample location. Control samples were collected to validate the heavy metal concentration in soil and labelled

control sample A and B from areas that are majorly residential area with low traffic volume and industrial activities. A total of twenty eight (28) soil samples were collected on the same day. The collected samples were stored in polyethylene bag and labeled properly and taken to the laboratory where the pH was immediately measured and recorded using digital analyzer model 61A pH-meter.

The collected soil samples were air-dried at room temperature, disaggregated in a ceramic pestle and mortar, and sieved through a 2 mm sieve to remove stones and pebbles. The <2 mm fraction of the soil was used for all soil analyses. Particle size distribution was determined by Bouyoucos hydrometer method [10] and pH was determined by Electric pH Meter with a direct readout. Calcium carbonate was measured by a volumetric method [11]. Organic matter was determined by the Walkley–Black procedure [12].

The total heavy metal content was determined using Mini Pal 4 version in PW 4030 X-ray Spectrometer according to Nelson [13] at Defence Industries Corporation of Nigeria, Research and Development Laboratory Kaduna. An aliquot (portion of sample) of finely ground soil was placed in a sample analysis cup. The sample cup was filled to three-quarters. The sample cup was then covered with a Mylar film before it was placed in the XRF machine. A voltage (30kV maximum and a current (1mA maximum) is applied to produce the X-rays to excite the sample for a preset time (10 minutes in this case). The entire data set of the analysis was made available on the monitor, displayed in percentage before it was converted to mgkg⁻¹.

2.1 Quality Control

As part of quality control measure to ensure reliability of results, samples were handled carefully to avoid contamination. Recovery test was carried out on the XRF machine by spiking analyzes.

Fig. 1. Map of kakuri industrial layout indicating soil sample collection points

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties

The results of the physicochemical analysis of soils from Kakuri industrial area are shown in (Table 1). The percentages of particle size distribution in the sample soil were in the range 7 to 15, 21 to 30 and 57 to 72% for clay, silt and sand respectively. Generally the soils were found to be sandy loam in majority of the areas and sandy in locations like IBB and SGA.

The pH result indicates the soil samples were slightly alkaline with values in the range 7.30 to 8.00 which is consistent with the value of 7.00 to 8.00 reported in literature [14]. The high soil pH values suggest that heavy metals availability for plant uptake is low in the sample soils.

The percent organic matter content was found to be in the range of 3.10 to 5.20 across the sample locations which is also consistent with the range 2.77 to 6.32 reported in literature [15], but was higher than the average value of 3.50 percent in the control samples. Hence, the relatively high total organic carbon content in samples soil as compared to control samples could be due to the high organic content of used lubricants that are discharged from heavy duty machines, mechanic workshops in the areas [16], as well as indiscriminate disposal of organic waste into the environment. It is also noted that the industrial area is crowed by residential houses with no proper waste disposal systems. The presence of organic matter has a significant effect on the mobility and bioavailability of heavy metals [17,18]. Furthermore, it has also been reported that about 50% of the total heavy metals in organic rich soils are retained with organic substances [19], but these values across the locations does not give an indication of a high tendency of heavy metals availability and retention in the soils around Kakuri industrial area.

3.2 Total Heavy Metal Concentration

X-ray fluorescence (XRF) analysis results for the collected soil samples shows presence of Zinc, Copper, Nickel, Chromium, Lead, Mercury and Vanadium for all the samples (Table 2).

3.2.1 Zinc

Zinc was detected in all the sample locations and depths across Kakuri Industrial layout with average concentration of 100.5±19.82 mgkg⁻¹ (Table 3) which is similar to the average value 108.67mgkg⁻¹ reported in literature [14]. These values are greater than the permissible value of 100 mgkg-1 of European standard [20], but less than the target and intervention values prescribed by Nigeria Department of Petroleum Resources [21] as displayed in (Fig. 2).

High concentration values of zinc may be due to natural occurrence of zinc in soil with about 70 mg kg−1 in crustal rocks [22]. Zn concentrations in most locations (UNT, AHT, RDQ, KTL, IBB and PAN) at both depths were found to be above 100mgkg^{-1} , with the exception of UNT where it was below 100 mgkg⁻¹ at 0 to 10 cm depth. This could be due to several smelting activities in these areas as well as from tyres and lubricant oil from high vehicular traffic along these locations. Indiscriminate disposal and combustion of zinc containing materials by resident in the area across the area also account for this.

3.2.2 Copper

Copper was present in all the sample locations. Its concentrations were greater than the permissible value 20 mgkg⁻¹of European standards [20] for all studied sites and depths including the control sites. It has an average value of 60.02 ± 3.60 mgkg⁻¹ (Table 3) across the twelve (12) sample locations. Copper distribution across the sample location was equally high with a wide range of 26 to 110mgkg $^{-1}$ but lower than the value of 98.00 ± 2.00 mgkg⁻¹ reported in literature [14].

The highest values were observed at AHT and KGW area with concentrations of 110 and 131mgkg⁻¹ respectively but did not exceed the DPR alert level of 120 mgkg⁻¹ as displayed in (Fig. 3). The lowest value of Cu was observed at NBC area with an average concentration of 26 mgkg⁻¹. High concentration of Cu in AHT was due to higher stability constant of Cu complexes with organic matter [23] indicating that it is mainly of lithogenic origin [24].

Table 1. Physicochemical parameters of samples and control soil in kakuri industrial area

CONT. A: Control sample A; CONT. B: Control sample B

Table 2. Concentration (mgkg-1) of heavy metals in soil samples

Table 3. Statistical summary showing Mean±SD, median and range of concentrations of heavy metals in soil samples

Results are presented as mean ± standard deviation, range and median across 12 sample locations in mgkg⁻¹

3.2.3 Nickel

Nickel (Ni) was detected in UNT, RDQ, KTL, AHT, ART, KGW and PGA locations with an average concentration of 26.25±6.44mgkg-1 (Table 3) across the twelve (12) sample locations. All the concentrations were greater than the permissible values 5mgkg⁻¹ for Ni according to the Romanian soil guidelines [20] but by far below 140.00mgkg⁻¹ stipulated by Nigeria Department of Petroleum Resources [21]. The highest concentration of Ni was observed around KGW area and ART (Fig. 2) due to activities around these locations which include Nickel plating in Kaduna machine and Defence Industries Corporation of Nigeria (DICON). Machines and power plants as well as trash incinerators may as well contributed to their presence in other locations across the industrial area.

3.2.4 Lead

Lead was detected only at KTL and PAN vicinity with an average concentration of 32.00±1.68 mgkg $^{-1}$ in the two areas which is higher than the mean values 20.02 ± 12.43 mgkg⁻¹ obtained by Umoru [25]. The concentrations in both locations were greater than the permissible value 20 mgkg $^{-1}$ at 10 – 20 cm depths (Fig. 3) but below the alert level of 50mgkg⁻¹ of European standards [20]. These concentrations were also slightly below the target value of 35mgkg⁻¹ and well below the value 210 mgkg $^{-1}$ intervention values by the Department of Petroleum Resources [21].

3.2.5 Vanadium

Vanadium was present in all the sample locations with an average concentration of 73.08 ± 3.52 mgkg⁻¹ which is greater than the permissible value 50 mgkg $^{-1}$ [20] for all studied sites and depths with the exception of AHT and NBC drive at 10 to 20cm depth with 47mgkg⁻¹ each (Fig. 3). None of the locations exceeded the intervention level of 120 mgkg as prescribed by DPR [21]. Vanadium was also widely distributed across the twelve locations with a range of 47 to 120 mgkg⁻¹ as it is known to have a natural occurrence average concentration of 135mgkg-1 [22,5].

3.2.6 Mercury

Mercury was detected in only three sample locations, UNT, AHT and IBB with concentrations is in the range 10 to 60 mgkg⁻¹. The highest concentration of mercury in soil was detected in AHT with an average of 60 mgkg⁻¹ (Fig. 3). This location houses several zinc, steel, aluminum and metal processing plants which are major sources of mercury in soil as well as release of mercury from manometer at pressure measuring sites and hydraulic lifts attached to trucks along AHT road. The slightly higher organic matter content of the soil at AHT and a high PH of 7.9 may also attribute to its presence in soil. The average values of Mercury in UNT and IBB were 18 mgkg⁻¹ and 25 mgkg⁻¹ respectively (Fig. 3). The concentrations of mercury in the three locations were found to be greater than the permissible level of 4mgkg⁻¹ specified in European guideline [20] but below the target value of 85mgkg⁻¹ stipulated by Department of Petroleum Resources [21].

Fig. 2. Concentrations of Zn, Cu and Ni at 10 to 20 cm depth of soil samples in comparison with average concentrations of control, DPR target and Intervention levels and RSG alert level *DPR TARGET: Department of Petroleum Resources Target Value DPR INT: Department of Petroleum Resources Intervention Value RSG ALERT: Romanian Soil Guideline Alert Level*

Fig. 3. Concentrations of Cr, Pb, V and Hg at 10 to 20 cm depth of the soil samples in comparison with average concentrations of control samples, DPR target and Intervention levels and RSG alert level

3.2.7 Chromium

Chromium concentrations across the sample $locations$ averaged 42.42 ± 5.2 mgkg greater which is less than the value of 93 mgkg⁻¹ reported by [14], but greater than the permissible value 30 mgkg⁻¹[20] for all studied sites and depths with the exception of UNT and AHT at 5cm depth with a concentration of 22 mgkg $^{-1}$ and 26mgkg-1respectively. Chromium was also detected in the control site B with an average of 31mgkg⁻¹. The highest concentration of 74mgkg⁻¹ was observed at CCG and KGW area due to the presence of DICON that engages in industrial activities such as heat and surface treatment that involves electroplating such as etching process and chrome plating [26].

The concentrations at all locations and level exceeded the target level of 20 mgkg $^{-1}$ but lower than the intervention level of 100 mgkg⁻¹ of the DPR soil classification [21] as displayed on (Fig. 3).

3.3 Heavy Metal Contamination in Soil

Assessments of heavy metals contamination in the sample soil were carried out using geoaccumulation and contamination factor pollution indexes.

3.3.1 Geo-accumulation index (Igeo)

This index allows the estimation of the enrichment of heavy metals concentration in soil above baseline concentration using an equation proposed by Muller, [27].

$$
I_{\rm geo} = \log_2\left(\frac{[M]}{1.5[M_b]}\right) \tag{1}
$$

Where

[M] = Measured concentration of heavy metals in sample soil

 $[M_b]$ = Geochemical background value of heavy metals in soil

The geochemical background value concentrations of heavy metals in soil are the average concentrations of the metals in the shale [28]. The I_{geo} index consists of seven grades (0 to 6) ranging from uncontaminated to highly and severely contaminated.

The results obtained from the studied areas indicates that the soil around Kakuri industrial area is generally uncontaminated with all the I_{gen} \leq 1 with the exception of only KGW with I_{geo} value of 1.561 for Zn measuring heavily contaminated with Zn (Table 3). This could be attributed to the large number of welding and machine works spread along this area.

3.3.2 Contamination factor (Cf) or enrichment ratio (ER)

The contamination factors are calculated according to the equation 2. The degree of contamination (C_d) was defined as the sum of all contamination factors. Calculated contamination factor (C_i) and degree of contamination (C_d) for this study is displayed in (Table 4).

$$
C_f = \frac{[M]}{[M_b]}
$$
 (2)

Where

[M] = Concentration of heavy metal in the studied area

 $[M_B]$ = Background concentration levels of metals in soil.

Background value of the metal is equal to world surface rock average given by [29]. The ER values between 0.5 and 1.5 indicates that the metals are entirely from the coastal materials whereas ER values greater than 1.5 indicates that the sources are most likely to be anthropogenic activities [30]. The different levels of degree of contamination based on the ER values are shown in (Table 5).

Results obtained are displayed in (Table 4). The soil of the studied area can be said to be moderately contaminated with Zn, Cu and Pb with mean values of 1.31, 1.40 and 1.70 respectively which falls under the classification 1 ≤ Cf< 3. The highest contamination of Zn (considerable contamination) was observed at KGW and RDQ for Zn. with values of 4.46 and 3.36 respectively. Pb was undetected in most of the sample locations with the exception of KTL and PEG with the same value of 1.7 which can be classified as moderate contamination.

On the basis of mean value of Cf, the soils are enriched for metals in the following order Cu > Pb $> Zn > Ni > Cr.$ Standard regulatory limits/background levels of metals in soil values.

3.4 Correlation Analysis of Soil Heavy Metals, pH and Organic Matter

Correlation coefficient measures the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympathetic relation). In this study, the raw data was used in calculating the correlation coefficient using the Microsoft Excel computer software package (Microsoft corp., 2013 version). The correlation analysis between heavy metals in sample soils, pH and organic matter (O.M) are shown in (Table 6). Some of the heavy metals are significantly correlated with each other as well as the pH and organic matter (O.M). Zn and Cu correlated positively with pH with values +0.41643 and +0.64447 respectively. This is an indication that pH is responsible for the availability of Zn and Cu in that soil which is evident from their availability in all the sample locations due to similar soil pH in the range of 7.30 to 8.00.

A positive correlation was observed between Zn and Cu $(+0.6142)$ and also Zn and Hg $(+0.6377)$ indicating that Zn have the same source(s) in the sample soils with Hg and Cu (Table 7). Humified organic matter is involved in the formation of soluble complexes especially with Zn and Cu which during organic mineralization become more available for the plants. This explains the higher availability of Cu in the studied soils and a strong correlation (+0.5920) with organic matter in relation to the other metals other than Zn.

Mercury (Hg) was only detected at UNT, AHT, and IBB where the O.M contents were highest and this is justified by the strong positive correlation value of +0.5355 with organic matter. Furthermore, there was strong negative correlation (-0.6255) between Hg and V indicating they have different source(s) of contamination in the environment.

Sample location	Enrichment ratio or contamination factor (C_i)							Degree of
	Zn	Cu	Ni	Cr	Pb	Hg	v	contamination
UNT	1.03	1.09	0.17	0.38		-	0.58	3.25
RDQ	3.36	1.51	0.49	0.38		٠	0.60	6.36
CCG	0.72	1.60	-	1.74		-	0.5	4.56
KTL	0.71	1.42	0.23	0.38	1.7	$\overline{}$	0.69	5.13
ART	1.36	1.84	1.06	0.44		$\overline{}$	0.69	5.39
AHT	0.73	2.44	0.62	0.38		٠	0.36	4.53
KGW	4.46	1.84	1.05	0.44		٠	0.69	8.48
NBC	0.73	0.57	$\overline{}$	0.42		٠	0.36	2.08
PEG	0.47	1.13	0.40	0.66	1.7	$\overline{}$	0.62	4.98
NCC	1.43	0.93		0.31		-	0.63	3.30
IBB	0.37	1.20	-	0.42		-	0.46	2.45
SNG	0.32	1.27	-	0.50			0.68	2.77
Mean	1.31	1.40	0.57	0.53	1.70		0.57	6.08

Table 5. Contamination factor (Cf) and degree of contamination (Cd) of soil samples in kakuri industrial area

Table 6. Mean concentration, baseline data (Mgkg-1), average shale (Mgkg-1), geo-accumulation index (Igeo) values and enrichment factor of heavy metals in soils in kakuri industrial area

** Superscripts to figures in the same column represent significant correlation at p<0.05 and * *Superscripts to figures in the same column represent significant negative correlation at p<-0.05*

4. CONCLUSION

The soil heavy metals (Zn, Cu, Ni, Cr, Pb, Hg and V) from the twelve selected locations in Kakuri industrial area was carried out in comparison with the control soil samples and the environmental soil guidelines. The results reveals that the locations UNT, RDQ, KTL, ART, AHT, KGW and PA were considerably polluted with heavy metals but still have heavy metal concentrations below the intervention/alert level provided by the environmental protection agencies. The results also shows that heavy metal availability and distribution pattern varies with industrial activities and this is indicated by the wide range of concentration values observed for virtually all the heavy metals in the soils analyzed across the sample locations. Soil pollution assessment using C_f and I_{geo} indices confirmed the soils are uncontaminated.

Therefore soils in Kakuri industrial area can be considered uncontaminated.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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